

TITLE OF THE INVENTION
HIGH TEMPERATURE RESISTANT COATING COMPOSITION

5

INVENTORS
Tuan Nguyenquang and Rong Jong Chang

10

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from a provisional patent application No. 60/448,657, filed 02/18/2003, the content of which is incorporated herein by reference.

15

FIELD OF THE INVENTION

The invention generally relates to a high temperature resistant coating composition. More particularly, it relates to a composition comprising mainly a mixture of a silicone resin (A), an epoxy resin (B), an amine curing agent (C), and a combination of fillers (D), which can be cured at ambient temperature to render it a tack free surface. After subsequent heat cure, the coating exhibits good film properties, high temperature resistance and undercut corrosion resistance.

20

DESCRIPTION OF THE BACKGROUND ART

Over the past 50 years, silicone resins have increasingly been used in the high temperature coatings. Listed below are several overview papers that provide a good introduction of the technology and an excellent summary of the background arts. The respective content of these papers is incorporated herein by reference.

25

1. Clive H. Hare, "Silicone Resins," JPCL (Journal of Protective Coatings and Linings), January 1995, pp. 79-103.
2. William A. Finzel, "Properties of High Temperature Silicone Coatings, JPCL, August 1987, pp. 38-43.

30

3. William A. Finzel, "Silicone Coatings, Generic Coating Types," JPCL, August 1995, pp. 93-106.

As described in the aforementioned references, the high temperature resistance of silicone resins has been attributed to its silicon-oxygen backbone in contrast with the carbon-carbon backbone for most organic polymers. A coating based on 100% silicone resin can resist up to 371°C. To achieve an even higher temperature performance, a platelet type of inorganic or metallic filler such as mica or aluminum flake is added to form a thermal reflective layer, and some filled silicone resin coatings can resist as high as 638°C (1200° F).

However, silicone resin based coatings for high temperature applications still suffer from several shortcomings. First, silicone resin is susceptible to chemical attack, particularly by sodium hydroxide, and if aluminum flake is used to raise the temperature performance, it reduces acid resistance of the coating. Second, a silicone resin based coating requires high temperature baking above 200°C to achieve the desired heat resistance properties. The coating can sag and run off during the heating process and thus leads to uneven or defective coating. Third, the silicone resin based coating is brittle and susceptible to cracking and lifting especially under thermal stress. This problem is particularly severe if the coating has poor adhesion or when its thickness is greater than three mils. Fourth, due to its inorganic nature, the coating properties such as gloss, impact resistance, toughness, or abrasion resistance are poor compared with most organic based coatings. Last, they have poor resistance to undercut corrosion, i.e., when there is pit corrosion developed due to imperfection in the coating, it quickly propagates underneath the coating.

To address some of the aforementioned shortcomings, one can modify silicone resin with organic components. The modification can be achieved by simply blending an organic resin with the silicone resins or by direct substitution of an reactive organic functionality onto the silicone resins, as described by Keijman, "The Use of Novel Siloxane Hybrid Polymers in Protective Coatings," PCE (Protective Coatings Europe), July 1996, pp. 26-32. Examples of chemically substituted silicone resins are Silikoftal® ED and Silikofal® EW, both of which are epoxy functionalized silicone resins supplied by Tego Chemie. The epoxy functionality

allows ambient curing when a suitable curing agent such as an amine is added to the composition to pre-cure the coating and thus prevents the coating from sagging or run-off during the subsequent baking at elevated temperatures.

5 By adding the organic content, the film forming properties and crack resistance are also improved. However, the increasing of organic content either by blending or functionalization normally compromises the heating resistance. The heat resistance of most organic modified silicone resin coatings is limited to 232°C-371°C, as noted in the Reference 2 cited above.

10 Thus, the challenge for the application of the silicone resin based coatings has been how to improve the film forming properties without sacrificing heat resistance. Muis disclosed in U.S. Patent No. 4,190,686 a composition comprising a ceramic glaze material, a thermosetting phenolic resin, an organic paint resin such as epoxy, polyester or acrylic and a silicone resin as leveling agent. The coating was either for protection steel from corrosion
15 and chemical attack or for protection of wood from fire. There was no mention of heat resistance; however, as it would have been apparent to any person skilled in the art, Muis's composition is unlikely to be suitable for a long-term exposure at temperatures greater than 200°C.

20 Arai disclosed in U.S. Paten No. 4,374,754 a self-cleaning coating composition containing a silicone resin, an organic solvent, an oxidation catalyst such as manganese oxide and/or platinum or palladium. The composition was designed to catalytically oxidize and remove fats and oils on interior surfaces of an oven, and it was claimed to resist temperature up to 600°C.

25 Matsumoto *et al.* disclosed in U.S. Patent No.'s 4,657,963 and 4,746,568 compositions consisting of a modified silicone resin, an aluminum chelate compound such as ethyl acetate aluminum diisopropylate, an organic resin, and a mixture of pulverized inorganic materials for use in coating exhaust pipes of motorcars. The compositions showed good film forming
30 properties and corrosion protection without compromising heat resistance.

Eklund *et al.* disclosed in U.S. Patent No. 6,180,726 a high temperature resistant powder coating composition comprising a resin containing functional hydroxyl groups, a polyfunctional epoxy resin, and an anhydride compound. The composition was claimed to withstand high temperature up to 300°C.

5

The prior patents cited above addressed some but not all of the aforementioned shortcomings of silicone resin based coatings. Therefore, there remains a need in the art for a high temperature resistant coating composition that overcomes all drawbacks of the prior arts.

10

SUMMARY OF THE INVENTION

Accordingly, it is the primary object of the present invention to provide an improved silicone resin based coating which can resist greater than 500°C temperature for long term uses.

15

It is another object of the present invention to provide an improved silicone resin based coating that can gel at ambient temperature to render it tack free for easy handling and inspection.

20

It is a further object of the present invention to provide an improved silicone resin based coating that can be baked at elevated temperatures without sagging or run-off on a vertical surface.

It is another object of the present invention to provide a silicone resin based coating that has improved coating properties.

25

It is still another object of the present invention to provide a silicone resin based coating with improved chemical resistance, particularly to sodium hydroxide.

It is yet another object of the present invention to provide a silicone resin based coating with improved resistance to undercut corrosion.

30

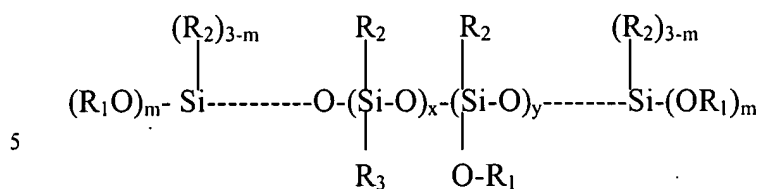
These objectives are achieved in a novel and inventive high temperature resistant coating composition comprising mainly a silicone resin, an epoxy resin, an amidoamine curing agent, and a mixture of three fillers: titanium dioxide, aluminum flake, and micaceous iron oxide that met all objects desired. The composition is particularly useful for protecting a kiln or baghouse in industrial facilities, such as a cement or power plant, from corrosion and chemical attack.

DESCRIPTION OF THE INVENTION

According to the present invention, the high temperature resistant coating composition consists of the following ingredients and their mass percentages. The total mass percentage of all ingredients must be 100%.

	Ingredient	Mass %
A	Silicone resin (without solvent)	10-17.5
15 B	Epoxy resin	3-15
C	Epoxy curing agent	6-30
D	Fillers	
	(1) Aluminum flake	1-10
	(2) Titanium dioxide	35-45
20 (3)	Micaceous iron oxide	7-20
	(4) Others (optional)	0-10
E	Catalyst (optional)	0-1
F	Additive (optional)	0-5
G	Solvent (optional)	0-7
25	Total 100.00	

The Component A, silicone resins, can be a straight or modified resin. In actual production, silicone resin may contain a certain amount of solvent, e.g., 20-35 mass parts of silicone resin with 50% in xylene. As one skilled in the art will appreciate, any amount of solvent may be used in actual production and is not limited to a 50% solution. The straight silicone resin has a general formula of:



where R_1 = either H, or CH_3 , or C_2H_5 ,

R_2 = an alkyl, acyclic, or aryl, preferably CH_3 or Phenyl ($-C_6H_5$),

10 R_3 = an alkyl, acyclic, or aryl, preferably CH_3 or Phenyl ($-C_6H_5$),

$R_2 = R_3$ or $R_2 \neq R_3$, and

$m = 1-3$, preferably 2, most preferably 3.

The combination of x and y determines the molecular weight of the resin, and either x or y
 15 can be from 1 up to several thousands. The ratio of y/x determines the cross-linking density of the final bake coating, and it can be from 20 for a high density network to 0.05 for a low density network. Preferably $(x+y)$ and y/x of the resin are low enough so that the resin is a liquid by itself, or can be dissolved in an organic solvent to form a liquid solution so that the final coating can be towed, brushed, or sprayed.

20

In the modified silicone resin, from 1% to 30% of R_2 is replaced with a reactive functional group such as epoxy, amine, vinyl, hydride, acrylic, anhydride, carboxylic, etc.

The silicone resins useful for the present invention can be a mixture of many straight silicon
 25 resins, or a mixture of straight silicone resins with up to 49% of modified silicone resins.

The Component B, epoxy resin, can be any bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, phenolic epoxy, phenol novolac epoxy, cresol novolac epoxy, tris(hydroxylphenyl) methane triglycidylether, triglycidyl p-aminophenol, tetraglycidyl
 30 amine of methylenedianiline, 1,3,5-tris(2,3-epoxypropyl)-1,3,5-perhydrotriazine-2,4,6-trione (triglycidyl isocyanurate), polyglycidylether of poly(4-hydroxystyrene), etc. It is preferable that B-1 be in a liquid form. If it is in solid form, a suitable solvent may be added to prepare a liquid solution. It is also understood that B-1 can be a mixture of various epoxy resins

mentioned above. It is preferable that the epoxy resin is a novolac epoxy due to its low viscosity and good chemical resistance.

5 The Component C is an amine curing agent or a mixture of amine curing agents for the Component B (epoxy resin). The curing agents include aliphatic amines, amidoamines, and cycloaliphatic amines. It is preferable to use amidoamines since they provide better adhesion to metal and also adequate pot life for the formulations. It is preferable that a stoichiometry amount of curing agent be used to react with the epoxy resin. However, a deviation of 15% from the stoichiometry amount will not significantly affect the coating properties of the
10 present invention.

The Component D is a mixture of fillers of mainly three fillers: aluminum flake, titanium dioxide, and micaceous oxide. Aluminum flake can be leafing or non-leafing type, preferably a non-leafing type. It can be in solid form or pre-dispersed in a paste form. Titanium dioxide
15 can be anatase or rutile type, preferably rutile type. Micaceous iron oxide refers to a crystalline form of iron oxide which naturally occurring in pallet form, which is very different from the more familiar red, yellow, and brown form of iron oxides. Optionally, other fillers such as mica, glass flakes, etc. can be added in small amount without significantly deteriorate the coating properties of the present invention.

20 The Component E is a catalyst optionally added to promote cross-linking reaction of silicone resin during high temperature bake. Most metallic organic salts such as zirconium octoate, cobalt octoate, zinc octoate, iron octoate, stannous octoate, or a commercial catalyst, such as K-Kat 348 supplied by King Industries, can be used. There are many known catalysts and
25 any person skilled in the art will have no problem choosing such a catalyst.

The Component F is additional additive(s) such as wetting agent, dispersing agent, deflocculating agent, thixotropic agent, defoaming agent, leveling agent, colorant, coupling agent, etc., that can be added to help dispersing of fillers, preventing filler settling, and
30 improving film forming properties or appearance.

The Component G is an organic solvent, optionally added to reduce viscosity of the mixture to facilitate coating application such as air spray or airless spray. The amount of solvent should be kept at a minimum, e.g., below 3.5 pounds per gallon of coating, preferably below 2.8 pounds per gallon, and most preferably below 1.8 pounds per gallon to reduce environmental pollution. Organic solvent selected must be compatible with silicone and epoxy resins. Toluene or xylene is often used with silicone resins.

To prepare the coating, a laboratory high speed disperser is used. Weigh titanium dioxide in a one-liter stainless container, and add silicone resin and epoxy resin. Let the mixture sit for 30 minutes. This will allow resins to soak into titanium dioxide. Mix the mixture with the high speed disperser at 4000 rpm and move the mixing blade up and down if necessary until the mixture is well dispersed. The mixture should achieve a reading of 7 or higher on the Hegman dispersion gauge. This process should take about 15-30 minutes. Add micaceous iron oxide and continue to mix at 4000 rpm for another 15-20 minutes until the mixture achieve a reading of 6 or higher on the Hegman gauge. Reduce the speed to 400 rpm and gently blend aluminum flake to the mixture. Close the lid of the container and let the whole mixture soak overnight (about 12-16 hours). Next, stir the mixture at 800 rpm for 15 minutes. Add solvent to obtain the Part A of the composition. Keep amine curing agent (Component C) separate as Part B of the composition. Part A and Part B are to be mixed just prior to coating application.

The following example shows a high temperature resistant coating composition prepared according to an embodiment of the present invention.

EXAMPLE 1

	<u>Ingredient</u>	<u>Description</u>	<u>Mass %</u>
A	Silikophen P50/X (Tego Chemie)	Silicone resin (50% in xylene)	25.96
B	Epalloy 8230 (CVC Specialty Chemicals)	Novolac Epoxy	6.49
C	Ancamide 2353	Polyamidoamine curing agent	13.41

	(Air Products)		
D	Fillers		
	(1) DF-L 520 AR	Aluminum flake	5.19
	(Silberline)		
5	(2) Tiona RCL-9	Titanium dioxide	42.18
	(Millenium)		
	(3) Nubifer EF	Micaceous iron oxide	13.32
	(Nubiola)		
G	Xylene	Solvent	3.37
10			Total 100.00

The high temperature resistant coating composition so prepared, applied in a 5-mil single layer on a steel panel (Q-Panel), became tack-free within 12 hours at room temperature. The coated panel was then cured at 250°C in a vertical position for one hour and no sagging or run-off was observed. After baking, the coated panel was quickly brought out of the oven and cooled down to ambient temperature. No delamination was observed during the thermal contraction. The baked coating showed high gloss and exhibited good scratch resistance.

The chemical resistance was tested by ASTM D471 by immersing a coating film in each of the test chemical for one week, and % weight gain was measured. It showed the weight gain in water, 36 % sulfuric acid, 54% phosphoric acid, and 50% sodium hydroxide was 0.8%, 1.1%, 1.2%, and 2.5%, respectively.

The baked coatings films were then subjected to long term heat aging at 250°C, 325°C, and 550°C. The baked films were taken out of the heating aging ovens weekly to simulate thermal cycling. The coatings resisted 325°C and 550°C up to three months without significant change in film properties and showed no cracking due to thermal cycling.

A baked film coated on a sand-blasted Q-Panel was also scribed and subjected to outdoor exposure with periodic spray of sodium chloride solution for two months according to ASTM D6675. The coating had very good resistance to undercut corrosion, having less than 0.5 mm

ingress of corrosion from the scribed line in one month. The adhesion of the coating remained good after the outdoor aging.

This working example demonstrated that the composition prepared according to the present invention is suitable for use in many applications as a high temperature resistant coating to protect steel from corrosion and chemical attack.

COMPARATIVE EXAMPLE 1

Instead of using a physical blend of epoxy resin with straight silicone resin, this comparative example was formulated with an epoxy modified silicone resin, in which the epoxy functional group was chemically attached to the silicone resin.

	Ingredient	Description	Mass %
A	Silikoftal ED (Tego Chemie)	Epoxy modified silocone resin	34.92
C	Ancamine 2089M	Modified Polyamine curing agent	5.82
D	Fillers		
	(1) Tiona RCL-9 (Millenium)	Rutile titanium oxide	45.04
	(2) Mica 20E (Fibertec)	Muscovite mica	14.32
			Total 100.00

A coating prepared according to the above formulation was applied onto a Q-Panel the same way as described in Example 1. The coating gelled and became tack free in 12 hours, and it was then baked in a vertical position at 250°C for one hour.

The baked coating films were then subjected to long term heat aging at 250°C, 325°C, and 550°C. The baked films were taken out of the heating aging ovens weekly to simulate thermal cycling. The coatings resisted 250°C aging for one week without cracking and delaminating, but at 325°C and 550°C they became powdery and eventually mud-cracked in

three days. This demonstrated that, unlike the present invention as shown in Example 1, the coating based on the epoxy modified silicone resin is not suitable for applications of temperature higher than 250°C.

5 COMPARATIVE EXAMPLE 2

A commercial silicone resin based coating was also selected for comparison with the present invention. The following formulation was recommended by GE Silicones in its technical data sheet, which is included herein by reference.

10	Ingredient	Description	Mass %
A	(1)Triplus 179	Methyl silsesquioxane resin	22.09
	(2)Triplus 178	Polydimethylsiloxane	18.07
	(GE Silicones)		
D	Fillers		
15	(1) Tiona RCL-9	Titanium oxide	45.38
	(Millenium)		
	(2) Mica 20E	Muscovite mica	14.46
	(Fibertec)		
E	K-Kat 348	Catalyst	0.004
20	(King Industries)		
			Total 100.00

A coating prepared according to the above formulation was applied onto a Q-Panel the same way as described in Example 1. The coating did not cure at ambient temperature and it
 25 sagged when applied on a vertical surface. Thus, the Q-Panel was placed in a horizontal position and baked at 250°C for one hour. The baked coating had a slightly powdery surface and the coating properties were not as good as that of Example 1.

The baked coating films were then subjected to long term heat aging at 250°C, 325°C, and
 30 550°C. The coatings were taken out of the heat aging ovens daily in the first week and weekly afterwards to simulate thermal cycling. The coatings resisted 250°C aging for 3

months without cracking or delaminating. However, the baked films appear powdery and the thickness should be kept below 2 mils to avoid cracking. At 325° C and 550°C, the coatings delaminated and cracked as soon as they were taken out of the ovens after one day. This demonstrated that the coating based on the blend of silicone resins is not suitable for applications of temperature higher than 250°C and therefore is substantially less versatile and useful than the present invention as shown in Example 1.

COMPARATIVE EXAMPLE 3 (SP7.A1)

This comparative example is to demonstrate the effect of the filler package.

10

	Ingredient	Description	Mass %
A	Silikophen P50/X	Phenyl methyl polysiloxane resin (50% in xylene)	26.95 (Tego Chemie)
B	Epalloy 8230 (CVC Specialty Chemicals)	Phenol Novolac epoxy	6.74
C	Ancamide 2353 (Air Products)	Modified polyamide curing agent	3.61
D	Fillers		
	(1) Tiona RCL-9 (Millenium)	Rutile titanium dioxide	44.99
	(2) Mica 20E (Fibertec)	Muscovite mica	14.21
G	Xylene	Solvent	3.50
Total			100.00

25

A coating prepared according to the above formulation was applied onto a Q-Panel the same way as described in Example 1. The coating gelled and became tack free in 12 hours. It was then baked at 250°C for one hour.

30

The baked films were then subjected to long term heat aging at 250°C, 325°C, and 550°C. The coatings were taken out of the heating aging ovens daily in the first week and weekly

afterwards to simulate thermal cycling. The coatings resisted 250°C and 325°C aging for three months without cracking and delaminating. However, the baked films appear powdery and the thickness should be kept below 2 mils to avoid cracking. At 550°C, the coatings delaminated and cracked as soon as they were taken out of the ovens after one day. This demonstrated that the coating based on the blend of silicone resins is not suitable for applications of temperature higher than 250°C and therefore is substantially less versatile and useful than the present invention as shown in Example 1.

COMPARATIVE EXAMPLE 4

This comparative example offers yet another demonstration of the filler effect.

	Ingredient	Description	Mass %
A	Silikophen P50/X	Phenyl methyl polysiloxane resin (50% in xylene)	28.00 (Tego Chemie)
B	Epalloy 8230	Phenol Novolac epoxy (CVC Specialty Chemicals)	7.00
C	Ancamide 2353	Modified polyamide curing agent (Air Products)	3.76
D	Fillers		
(1)	Tiona RCL-9	Rutile titanium dioxide (Millenium)	37.40
(2)	Mica 20E	Muscovite mica (Fibertec)	11.81
(3)	REF-160	Microglas glass flake (NGF Canada)	8.40
G	Xylene	Solvent	3.64
Total			100.00

A coating prepared according to the above formulation was applied onto a Q-Panel the same way as described in Example 1. The coating gelled and became tack free in 12 hours, and it

was then baked at 250°C for one hour. When the baked coating was subjected to 50% sodium hydroxide, it was totally dissolved in a few days.

The baked films were then subjected to long-term heat aging at 250°C, 325°C, and 550°C. 5 The coatings were taken out of the heating aging ovens daily in the first week and weekly afterwards to simulate thermal cycling. The coatings resisted 250°C and 325° C aging for three months without cracking and delaminating. However, the baked films appear powdery and the thickness should be kept below 2 mils to avoid cracking. At 550°C, the coatings delaminated and cracked as soon as they were taken out of the ovens after one day. This 10 demonstrated that the coating based on the blend of silicone resins is not suitable for applications of temperature higher than 325°C and therefore is substantially less versatile and useful than the present invention as shown in Example 1.

Although the present invention and its advantages have been described in detail, it should be 15 understood that the present invention is not limited to or defined by what is shown or discussed herein. The tables, description and discussion herein illustrate technologies related to the invention, show examples of the invention and provide examples of using the invention. Known methods, procedures, systems, elements, or components may be discussed without giving details, so to avoid obscuring the principles of the invention. One skilled in 20 the art will realize that implementations of the present invention could be made without departing from the principles, spirit, or legal scope of the present invention. Accordingly, the scope of the present invention should be determined by the following claims and their legal equivalents.